

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 2001-001645

(43)Date of publication of application : 09.01.2001

(51)Int.Cl.

B41M 5/26

B41M 5/34

(21)Application number : 11-178743

(71)Applicant : GUNZE LTD

(22)Date of filing : 24.06.1999

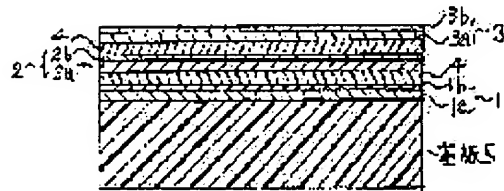
(72)Inventor : TONOI KAZUTO  
OKAMOTO TOSHINORI  
TANAKA AKIHIRO

(54) THERMALLY REVERSIBLE MULTIPLE COLOR RECORDING MEDIUM

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a new reversible multiple color recording medium by which a more accurate, finer and clearer multiple color image can be expressed, and wherein a re-writing can be freely performed by deleting the image.

SOLUTION: A writing is performed by using at least three laser beams, and this thermally reversible multiple color recording medium is constituted by laminating at least following three layers of respective thermally reversible color recording layers (A) to (C) on a base sheet 5. That is, the thermally reversible multiple color recording medium comprises (A) a thermally reversible color recording layer 1 comprising a first thermally reversible color developing layer 1a and a first laser beam absorbing layer 1b having a wavelength to develop a color of the color developing layer, (B) a thermally reversible color recording layer 2 comprising a second thermally reversible color developing layer 2a and a second layer beam absorbing layer 2b having a



wavelength to develop a color of the color developing layer, and (C) a thermally reversible color recording layer 3 comprising a third thermally reversible color developing layer 3a and a third laser beam absorbing layer 3b having a wavelength to develop a color of the color developing layer. More preferably, a transparent heat insulating layer (glass bead or the like) is inserted between the recording layers 1 and 2, and 2 and 3. A multiple color recording/deletion is performed with colors of red, blue, green and the like.

## DETAILED DESCRIPTION

---

### [Detailed Description of the Invention]

[0001]

**[Field of the Invention]** Especially this invention relates to the improved heat-reversibility multicolor record medium suitable for laser writing. This self can be used for the various advertising media whose rewriting is possible, or this record medium can also coalesce and use it for rewriting or the various possible cards of a reuse.

[0002]

**[Description of the Prior Art]** general -- a reversibility record medium -- the Society of Electrophotography of Japan -- there are two, the case where an image expression is carried out in the monochrome of only nebula by making a physical change into a principle, and when an image expression is carried out with multiple color by making a chemical change into a principle, so that it may be, even if special edition description is given as "latest trend of a RIRAITA bloomers king technique" at volume [ 35th ] No. 3 (1996) and 148-154 pages. Although this is made into a card system and it has already used in the reversibility (lilac ITABURU) record medium by the former monochrome in 1 section gas station etc., the present condition is not being the phase of practical use yet in the reversibility record medium by the latter multiple color. It is thought that research is advanced and they go as a future big theme since the needs of colorization are high.

[0003] JP,8-80682,A can be mentioned as a technique in recent years seen by patent application about a reversibility multicolor record medium. The basic technical thought of this official report uses as a lower layer the coloring layer which consists of one layer containing two or more irreversible colors (the color or the organic pigment currently generally used for printing ink) which absorb a wavelength light peculiar to the color respectively, and generate heat, carries out the laminating of the lilac ITABURU layer reversibly changed on it at transparency or non-transparency (nebula) at specific temperature (temperature by generation of heat of this irreversible color), and is taken as a reversibility multicolor record medium. The coloring layer which consists of this one layer here is divided into each pigmented layer, this lilac ITABURU layer is prepared on it for every pigmented layer, the laminating of this is respectively carried out through the thermal break (air) of translucency, and the purport good also as this record medium is also indicated.

[0004]

**[Problem(s) to be Solved by the Invention]** this invention persons have examined many things from another different include angle from said number official report. Consequently, the reversibility multicolor record medium which was excellent also in endurance in a clearer multi-colored picture image being could be found out, and this invention was reached.

[0005]

**[Means for Solving the Problem]** That is, this invention makes a main means the heat-reversibility multicolor record medium which the laminating of the three layers of each heat reversible color recording layer of following (A) - (C) is carried out, and becomes at least on a substrate (5) so that it may indicate to claim 1 first.

(A) The heat reversible color recording layer which consists of the 1st heat reversible color coloring layer (1a) and an absorption layer (1b) of the 1st laser beam which has the wavelength for coloring of this coloring layer (1)

(B) The heat reversible color recording layer which consists of an absorption layer (2b) of the 2nd laser beam which has the wavelength for coloring of the 2nd heat reversible color coloring layer (2a) and this coloring layer (2)

(C) The heat reversible color recording layer which consists of the 3rd heat reversible color coloring layer (3a) and an absorption layer (3b) of the 3rd laser beam which has the wavelength for coloring of this coloring layer (3)

[0006] And invention of claim 2 is also offered in relation to said main patent. It is the heat-reversibility multicolor record medium characterized by carrying out the laminating of the transparence thermal break (4) further between the layers of said heat reversible color recording layer (1, 2, 3) of at least three layers by which a laminating is carried out. This transparence thermal break (4) prepares as a desirable gestalt here with the detailed glass bead implanted in the shape of a dot by 5-100 micrometers in thickness, and it is \*\*\*\*\* (claim 3).

[0007] Moreover, invention which is subordinate to said claim 1 or 2, and is indicated to claims 4, 5, and 6 is also offered. This invention is explained in full detail with the following operation gestalt below.

[0008]

**[Embodiment of the Invention]** First, the heat-reversibility multicolor record medium (it is called a HRC medium below.) of this invention writes in a certain information freely using three laser (light) with which wavelength differs at least, and expresses the written-in information quickly by the image of three or more colors (development). Conversely, if this is quenched at a certain temperature or gradual cooling is carried out, the expression color picture will be maintained as it is, or it will be eliminated. Repeat actuation of this expression and elimination can be performed, that is, it can be said to be what made possible the RIRAITA bull color information record medium by the new configuration.

[0009] Writing is specified as the laser beam especially here as compared with the approach of writing in by the thermal emission from other thermal heads, the MAG, electric field, a pressure, etc., because I hear that a more detailed image can arrange in the state of being written in quickly more vividly and non-contact and there is also no danger, such as dirt and damage.

[0010] Then, based on claim 1, it explains on what kind of configuration the HRC medium by said at least three laser beams which can be written in is based.

[0011] First, a HRC medium is formed on a substrate 5, in order to make it easy (on manufacture and use) to be safe and to deal with it. The use gestalten (a material, thickness, transparence - opacity, application, etc.) of this substrate are as follows. About a material, inorganic sheet-like objects, such as a sheet-like object by thermosetting resin, such as a sheet-like object by the

thermoplastics of crystallinity, such as the paper board, a synthetic paper, the nonwoven fabric by the synthetic fiber, polyethylene terephthalate, polyethylenenaphthalate, a polyether ketone, a polycarbonate, polymethylmethacrylate, annular polyolefine, polyether sulphone, and polyarylate, or amorphism nature, an epoxy system, acrylic, an urethane system, and an imide system, a ceramic, and glass, are mentioned, for example. of course -- these -- proper -- you may be the compound sheet which compounded two or more sorts. Generally such thickness is set to about 0.1-3mm. Moreover, about transparence - (translucent) - opacity, especially this is decided by relation with an application. For example, for applications like a display, such as a poster, an opaque sheet is chosen in coalesce with transparence thru/or a translucent sheet, and various cards. case [ and ] these are transparent -- no coloring -- it is -- translucent - when opaque, it is desirable that it is a white system. Whitening has approaches, such as a scour lump by titanium oxide or surface coating, and surface roughening. In addition, in order to give an adhesive property to said sheet, you may pretreat by physical (corona discharge etc.) and the chemical approaches (scaling by the oxidizer etc.), and if, an anchor coat layer may be prepared.

[0012] And although the laminating of the heat reversible color recording layer (1) of (A) - (C), (2), and (3) is carried out respectively independently at least on said substrate 5, this is for carrying out an image expression by three colors respectively at least using three laser beams from which wavelength differs at least. Therefore, calling the 1st and (B) the 2nd, and having especially called (C) the 3rd does not call (A) in order [ these ] to distinguish to three, even if few, and the sequence of a laminating (this recording layer-hue) is not said [ expedient ], either. As for the built-up sequence of a \*\*\*\* recording layer, it is desirable to use a dark color system as the lowest layer from the point of improvement, to turn the laminating of the light color up one by one, and to make it consist of that of visibility. For example, in the case of three hues of red, blue, green, or yellow, blue is made the lowest layer and green or yellow is made an interlayer for red at the maximum upper layer.

[0013] Said heat [ in / at least / the 1st, the 2nd, and the 3rd ] reversible color recording layer (1, 2, 3) consists of a heat reversible color coloring layer (1a, 2a, 3a) and a laser beam absorption layer (1b, 2b, 3b) corresponding to each. Next, each of this pigmented layer from \*\* and an absorption layer are explained in full detail.

[0014] First, when carry out a color expression by red, blue, and three green hues, said each heat reversible color coloring layer use as a principal component both of the electronic receptiveness compound ( it be call a developer below.) which carry out a \*\*\*\* operation with temperature to the precursor ( it be call the color coupler below.) and this color coupler of the electron-donative color which be each source of coloring, it mix this to binder resin, distribute, and make them each \*\*\*\*. For existence of this resin, it is [ discharge / coloring and ] more desirable for there to be nothing from the field of a clearer and faithful repeat operation here. However, in order to distribute a color coupler and a developer to homogeneity and to make adhesion with a substrate 5 firm, concomitant use of this resin is desirable. However, the thing little as much as possible of the amount of presentations is desirable.

[0015] As said color coupler, they are fluoran lactone compounds, such as 2-clo low 6-diethylamino fluoran lactone and 3-MECHIRU 6-diethylamino fluoran lactone, for example at red. If blue, they are phthalide system compounds, such as 3-(4-diethylamino 2-methylphenyl)-3-

(1-ECHIRU 2-methylindole 3-IRU)-4-aza-phthalide and 3-(4-diethylamino 6-ethoxy phenyl)-3-(1-hexyl 2-methylindole 3-IRU)-4-aza-phthalide. If green, they are fluoran lactone compounds, such as 7-(N and N-dibenzylamino)-3-(N and N-diethylamino) fluoran lactone and 7-(N-octyl amino)-3-(N and N-diethylamino) fluoran lactone. Otherwise, in yellow, fluoran lactone compounds, such as 3-methoxy 6-methoxy fluoran lactone, can be illustrated, and, black, fluoran lactone compounds, such as 7-(2-KURORU phenylamino)-3-(diethylamino) fluoran lactone and 6-methyl-7-(2, 4-dimethyl phenylamino)-3-(diethylamino) fluoran lactone, can be illustrated. Of course, by the ordinary state, these are carrying out colorlessness or light coloring, and differ from the color for ink and pigment which are respectively colored by the ordinary state.

[0016] Moreover, there is especially nothing that will be restricted if said developer is a compound which doubles and has fundamentally a part for a part for the structured division which shows the development ability which makes said color coupler color, and the long-chain aliphatic series structured division which controls the cohesive force between molecules. For example, in a part for the structured division which shows this development ability, it is a phosphoric-acid radical, a carboxylic-acid radical, an aromatic series radical, etc., and is the long-chain alkyl group of C12-C24 preferably ten or more carbon numbers C in a part for the structured division which controls this cohesive force. When a concrete compound is illustrated, an N-BEHENIROIRU 4-aminophenol, p-(octadecyl thio) phenol, p-(EIKO sill oxy-) phenol, Long-chain alkyl aromatic series system compounds, such as p-hexadecyl carbamoyl FENIRU and 4-(N-behenoyl amino) phenoxyacetic acid, alpha-hydroxy hexadecanoic acid, 2-BUROMO hexadecanoic acid, 3-oxo-octadecanoic acid, Long-chain alkyl phosphoric-acid compounds, such as long-chain alkyl monochrome, such as an octadecyl malic acid, octadecyl thiophosphoric acid, and 2-octadecyl pen TANIN acid, or a dicarboxylic acid compound, octadecyl phosphonic acid, and EIKO sill phosphonic acid, etc. can be mentioned.

[0017] Moreover, it is good to choose [ being called the resin which is compatible to a color coupler and a developer as said binder resin first, is excellent in adhesion with a substrate 5, dissolves in a solvent (water or organic solvent), and is excellent also in the transparence of itself, a heatproof, and weatherability ]. Although various resin which suits the resin of these conditions is considered, choosing in the thermoplastic polymer of amorphism nature is more desirable.

[0018] The thermoplastic polymer of the amorphism nature as said binder resin For example, the copolymerization polymer of a polyvinyl chloride, polyvinyl acetate, a polyvinyl chloride, and vinyl acetate, Polystyrene or the copolymerization polymer of this and other vinyl monomers, the copolymerization polymer of independent or this acrylic and other acrylic vinyl monomers, Vinyl system polymers, such as a maleic-acid system copolymerization polymer, a polyvinyl alcohol system polymer, and an annular olefin system polymer, A phenoxy polymer, polyurethane, a polycarbonate, an ester system polymer (amorphia), a semisynthesis cellulose (ethyl cellulose, hydroxyethyl cellulose, carboxymethyl cellulose), starch, etc. can be mentioned. In addition, when daring use a crystalline thermoplastic polymer, degree of crystallinity is low as much as possible, and it is good to choose what has the low melting point.

[0019] although the presentation rate of said which color coupler which constitutes said each heat reversible color coloring layer, a developer, and binder resin is good to take various

conditions into consideration and for preliminary experiment to determine -- a profile -- it is as follows. 15 - 40 % of the weight of color couplers, 85 - 60 % of the weight of developers, and binder resin are 1 - 10 % of the weight to the total quantity of a color coupler and a developer. In addition, minute amount addition of additives, such as a sensitizer which is used for a dispersant, a surfactant, lubricant, an antioxidant, an ultraviolet ray absorbent, light stabilizer, a coloring stabilizer, a decolorization accelerator, and a common thermal paper for improvements, such as the formation property of this coloring layer and coloring/decolorization property, is permitted.

[0020] And generally as for the means forming to the substrate top of each of said heat reversible color coloring layer, the following approach is taken. The resin binder of the amount of requests is first dissolved in an organic solvent. Since the amount of dissolutions changes with the solubility and the formation approaches for this resin and it is not decided uniquely, it is good to decide by the preliminary test. Next, separate or the thing \*\*\*\*\* mixed is respectively added for the initial complement of a predetermined color coupler and a predetermined developer in the dissolved solution. After addition is fully stirred and distributes the whole to homogeneity. Here, there is no limit in mixed conditions and a mixed sequence foreword. And it applies to predetermined thickness with coating means (SUPINKO-TEINGU, roll coating, \*\*\*\*\*\_\*\*\_TENIGU, screen printing, etc.), and dries.

[0021] As for the thickness of each of said coloring layer coated here, it is desirable to change by whether it makes into an interlayer whether to make this into the lowest layer or it is made the maximum upper layer. This is because it will become easy to come to the coloring concentration of the image which worsens transparency of a laser beam and is displayed as a result, the Sharp difference, etc. out of a bad influence if the upper layer is thick. therefore -- \*\* -- saying and making it too much thin will lower coloring concentration of a layer own [ the ]. Therefore, although it is good to decide by the prior check with careful attention to this thing, preferably, the range which can generally be said is 5-20 micrometers, and finds out the 1-30 micrometers of the optimal thickness for each coloring layer in this.

[0022] Next, the absorption layer (1b) of the 1st, 2, and 3 laser beam prepared corresponding to said each heat reversible color coloring layer (1a) (2a) (3a), (2b), and (3b) are explained in full detail.

[0023] Said each absorption layer is required for it to be efficient and transmit [ absorb quickly the 1st, 2nd, or 3rd laser beam from which wavelength differs respectively, change into heat (predetermined temperature) and ] this in each the layer of said coloring faithfully. Therefore, it will be decided by what kind of hue this absorption layer makes this coloring layer, and a laser beam (wavelength) will also be decided. This will also become that this absorption layer and this coloring layer to it decided, if the wavelength of each laser beam to be used is decided conversely. The tint of a \*\*\*\* absorption layer and the tint of a coloring layer are good to make it double as much as possible.

[0024] The laser beam used first here is chosen and it is still better that the wavelength what generally has preferably about 600-1000nm of 650-900nm wavelength regions was decided to be within this wavelength is single wavelength as much as possible. The generation source of a \*\*\*\* laser beam has the desirable semiconductor laser of about 20mW of optical outputs

especially, although gas laser, fixed laser, semiconductor laser, etc. are applicable.

[0025] And said each absorption layer to said each decided laser beam is specifically the thing of the following contents. First, this layer is alternatively efficient, absorbs the wavelength from the selected laser beam, and a laser beam absorbent convertible into predetermined heat (temperature) energy as it serves as a principal component, and it is formed. More effective selection of this absorbent is that it is desirable to also take a molar extinction coefficient into consideration further here, although decided of course in consideration of the effect of the coloring chromaticity on said each decided coloring layer, endurance (thermal resistance to repetitive heating and cooling), film production nature, adhesion with a coloring layer, etc.

[0026] the strength of absorption in the range of 600-1000nm (visible being and carrying out infrared wavelength) where said absorbent molecule is emitted from a laser beam in this invention although said molar extinction coefficient (it is also called a molar extinction coefficient.) is generally expressed as the strength to which a coloring matter molecule absorbs light -- \*\* -- it will say. And this is JIS. It can measure with the spectrophotometry indicated by K0212. If this molar extinction coefficient is also considered and it will also put [ as opposed to / in / this absorbent / figure / 10000 or more laser beam absorbents and the laser beam which are these 20000 or more absorbents more preferably, and is specified further ] into conditions that the width of face of an absorption wavelength peak is a thing 200nm or less, a much more desirable infrared absorption agent can be chosen.

[0027] When said target laser beam absorbent is illustrated to a system category, this absorbent that absorbs only thermal-conversion wavelength peculiar to coloring of said coloring layer based on said conditions further in this will be chosen by the cyanine system generally known, a phthalocyanine system, the India cyanine system, a naphthalocyanine system, an anthraquinone system, a poly methine system, the aminium system, the potato NIUMU system, the dithiol system, a metal complex system, etc.

[0028] It is as follows when means forming is illustrated to said each coloring layer (1a) to said each absorption layer (1b), (2b), and (3b), (2a), and a top (3a). The specified quantity is dissolved in an organic solvent as it is, or at least three sorts of laser beam absorbents chosen first are dissolved with little coexistence of said binder resin, and each coating liquid is adjusted. Next, this each whole corresponding coloring layer top surface is coated with this each coating liquid by the coating approach (either which is illustrated in the case of said coloring layer). Stoving of after coating is carried out, it carries out evaporation removal of the organic solvent, and is completed. It is desirable to take into consideration and decide various conditions (for effect in the coloring layer by coloring of the absorbent itself to be [ strong against laser beam absorbing power and an impact the adhesion force and endurance endurance, ] still smaller) about the thickness of each of this absorption layer finally obtained by coating here, and it is good to decide in this by making about 0.1 micrometers - 5 micrometers into a standard. in addition, generally about an organic solvent, ether (between the shape of a chain -- or annular), fatty alcohol, ketones (the shape of a chain -- or annular), aliphatic series ester, aliphatic series nitril, and chlorinated methane are used. Moreover, it is more desirable not to \*\*\*\*\* as much as possible, since it generally tends to worsen concomitant use of binder resin in respect of the absorption efficiency of a laser beam, the heat-conduction effectiveness to a coloring layer, the

absorption peak width of face (direction to extend) of an infrared-absorption agent, etc. Especially when using it, it is good film reinforcement and to restrict, when not obtaining any longer in respect of membrane formation nature, and to make it as little as moreover possible.

[0029] Although the direct laminating of said each heat reversible color recording layer (1), (2), and (3) will be carried out one by one on a substrate 5 and they will obtain the target heat-reversibility record medium, they once prepare this each recording layer in films, such as PET thinner than this substrate, carry out each laminating of this, and are fundamentally good also as this record medium.

[0030] Moreover, although it is a more desirable thing that it is what can record more quickly that a still clearer color image is also efficiently, and can also do a discharge, claim 2 is offered as a means for it and solution is aimed at It is said that this account means makes at least two transparence thermal breaks (4) intervene between the layers of the heat reversible color recording layer (1) which consists of at least three layers in claim 1, (2), and (3) (i.e., between (1) and (2)), and between (2) and (3). Since this transparence thermal break carries out the operation which insulates between these recording layers, heat propagation-comes to be hard of a thermal break. That is, it is used for coloring as it is, without otherwise the heat uniquely received by this recording layer of this recording layer that adjoins respectively escaping. Since affecting coloring of this recording layer that adjoins as a result, and a discharge is mitigated, a clearer color image comes to be reproduced correctly quickly. Moreover, the endurance of repeat use also improves more.

[0031] Said transparence thermal break (4) considers as about 5-100-micrometer thickness, and is specifically formed with a glass bead with a particle size of about 2-40 micrometers which forms this by the air space or contains transparence adhesive property resin etc. In the case of an air space, there are approaches, such as putting a spacer into a perimeter, considering as an entire air space, or it being extensively scattered and making a dot (point) spacer (based on transparence binder resin) with a height of 5-100 micrometers into an air space, here so that a 5-100-micrometer clearance may be vacant. Especially in the case of the latter, since an air space is certainly formed in the size of a heat-reversibility multicolor record medium not related, it is desirable. When based on a \*\*\*\* glass bead, this glass bead is mixed with an organic solvent using a small amount of possible transparence adhesive property resin, and the coating (implantation) of this is carried out so that it may be extensively scattered by the detailed dot. Since it is certainly regardless of the thickness for which it asks also in this easy also for formation in the size of this record medium, it is this glass bead, and the approach of implanting this in the shape of dispersion by the dot, and forming is still more desirable.

[0032] In addition, although said obtained heat-reversibility multicolor record medium is used as it is Protecting the laser beam absorption layer which is in the maximum upper layer at least (protection from damage in environmental ambient atmospheres, such as air, water, and temperature, use, and a routing etc.) Since it is desirable, for the reason, it is transparent as much as possible, and it also good to cover extensively [ about 0.1-10 micrometers of thickness ] the material which also penetrates a laser beam well (it does not absorb). Although specification is not carried out as this material, when being based on resin, the coating of the precursors, such as the transparence resin of a photoresist, for example, acrylic, an epoxy system, an urethane



system, an acrylic epoxy system that combines a silicone component, an acrylic urethane system, and an acrylic silicone system, is carried out, and they carry out photo-curing. On the other hand, the silicon oxide film by the sol-gel method, the oxidization silicon film by the sputtering method, or the ITO (indium stannic acid ghost) film can also be used as a protective coat. Although it is not influenced by \*\* and decolorization operation even if it, of course, prepares the protective layer by these, this is also because this invention changes by the specific configuration, and it is \*\*.

[0033]

[Example] This invention is further explained in full detail according to an example with the example of a comparison below. In addition, whenever [ as used in the field of in this example / coloring ] is measured by the following approach, and is expressed with a  $L^*a^*b^*$  color coordinate system. That is, JIS Irradiate the laser beam corresponding to red first, the red who did the laminating and got on the white substrate in each example, blue, and a green heat reversible 3 color record plate (medium) are made to color red using the color color difference meter "CR-200" by Minolta Co., Ltd. currently manufactured based on Z8729, and  $L^*a^*b^*$  of this is measured. If measurement finishes, it will heat to 80-degreeC and red will be decolorized. Next, the laser beam corresponding to blue is irradiated and it colors similarly. - It measures. - It decolorizes. The laser beam which corresponds to the last green is irradiated, and it colors, measures - decolorizes similarly.  $L^*$  is so light that a figure is large at the lightness index of each color, and lacks in thickness here (if conversely small, it will become deep and will become blackish).  $a^*b^*$  is the chromaticity which shows a hue and \*\*\*\*\* and, in the green direction and  $b^*$ , the direction of yellow and  $-b^*$  indicate [  $a^*$  / the direction of red, and  $-a^*$  ] that the direction of blue is clear from a  $L^*a^*b^*$  color-coordinate-system chromaticity diagram.

[0034] (Example 1) Red, blue, and the green presentation liquid for heat reversible color coloring layers were first prepared by the next formula.

For red coloring: As a heat-reversibility red color coupler, the water-solution 90 weight section of 2.5% of the weight of polyvinyl alcohol was added to 40 weight sections and this, and mixed distribution of the 2-chloro-6-diethylamino fluoro lactone fine particles was fully carried out (A liquid). On the other hand, as a developer, 2.5% of the weight of the polyvinyl alcohol water-solution 400 weight section was added to the 100 weight sections and this, and mixed distribution of the N-BEHENI roil aminophenol fine particles was fully carried out (B liquid). And this A liquid 65 weight section and this B liquid 250 weight section were extracted, and the water-solution 100 weight section of 10% of the weight of polyvinyl alcohol and the water 200 weight section were added to this, and it fully mixed, and considered as the presentation liquid for red coloring (red coloring liquid).

For blue coloring: It changed to said red color coupler, and except using 3-(4-diethylamino-2-methylphenyl)-3-(1-ethyl-2-methylindole-3-IRU)-4-aza-phthalide as a reversibility blue color coupler, it each prepared on the same conditions as the above, and the presentation liquid for blue coloring was obtained (blue coloring liquid).

Green coloring: It changed to said red color coupler, and as a reversibility green color coupler, except using 7-(N and N-dibenzylamino)-3-(N and N-diethylamino) fluoro lactone, it each prepared on the same conditions as the above, and the presentation liquid for green coloring was obtained (green coloring liquid).

[0035] On the other hand, the presentation liquid for laser beam absorption layers corresponding to said each coloring layer was prepared by the next formula.

For red absorption: 0.1g of phthalocyanine system absorbents which absorb the wavelength of the 830nm of the maximum absorption peaks by absorption peak width of face of 50nm was dissolved in 20g of ethyl acetate (red lean solution).

For blue absorption: 0.1g of phthalocyanine system absorbents which absorb the wavelength of the 655nm of the maximum absorption peaks by absorption peak width of face of 50nm was dissolved in 20g of ethyl acetate (blue lean solution).

For green absorption: 0.1g of phthalocyanine system absorbents which absorb the wavelength of the 780nm of the maximum absorption peaks by absorption peak width of face of 50nm was dissolved in 20g of ethyl acetate (green lean solution).

[0036] Next, the heat-reversibility record object of three colors which carry out coating one by one, carry out the laminating of said each presentation liquid for heat reversible color coloring layers and the presentation liquid for laser beam absorption layers, and ask for them in the following procedure on this was produced by using a white opaque PET film ( $L^*=99.44$ ,  $a^*=-0.57$ ,  $b^*=0.19$ ) with a thickness of 125 micrometers as a substrate 5. First, said red coloring liquid was applied, it dried, and 1st 10-micrometer heat reversible red coloring layer 1a was prepared, next, on this 1a, said red lean solution was applied, it dried, 1st 1-micrometer laser beam absorption layer 1b was prepared in the whole surface of this PET film, and it considered as the 1st heat reversible red recording layer 1. Next, on the heat reversible red recording layer 1, said blue coloring liquid was applied, it dried, and 2nd 10-micrometer heat reversible blue coloring layer 2a was prepared, succeedingly, said blue lean solution was applied, it dried, 2nd laser beam absorption layer 2b of 1 micrometer was prepared on this 2a, and it considered as the 2nd heat reversible red recording layer 2. And said green coloring liquid was applied to the last on this heat reversible red recording layer 2, it dried, and 3rd 10-micrometer heat reversible blue coloring layer 3a was prepared, and on this 3a, said green lean solution was applied, it dried, 3rd 1-micrometer laser beam absorption layer 3b was prepared in the continuation, and it considered as the 3rd heat reversible green recording layer 3.

[0037] And coloring and a discharge were tested in red, blue, and green order about the heat-reversibility record object of said three produced colors, and the engine performance was checked. Coloring performed green coloring here because red coloring irradiates respectively separately the semiconductor laser light to which blue coloring has maximum single wavelength in 655nm respectively at 780nm from this record object at 830nm. After the discharge colored and measured  $L^*a^*b^*$  whenever [ coloring ], before it performed the next coloring, it was performed by making it 80-degreeC. Each color was colored efficiently and the result decolorized it again. Whenever [ coloring / at that time ] was summarized in Table 1. Although  $L^*a^*b^*$ -ization was measured whenever [ coloring / of each color ] when it was attached to \*\*\*\*\* and coloring and a discharge were repeated 100 times, there was no difference between the beginnings (Table 1).

[0038] (Table 1)

実施例 NO	発色	L*	a*	b*
1	赤	84.53	18.40	16.23
	青	89.65	-4.99	-8.86
	緑	63.47	-12.20	6.05
2	赤	82.95	20.43	16.34
	青	88.82	-6.48	-9.21
	緑	60.18	-14.37	6.21

[0039] (Example 2) (example of claim 2)

Said red coloring liquid, blue coloring liquid, green coloring liquid and the red lean solution, the blue lean solution, and the green lean solution were first prepared on the same conditions as an example 1.

[0040] The transparence acrylic resin precursor liquid (liquid for thermal breaks) of the photoresist which, on the other hand, contains 20 % of the weight for a glass bead with a particle size of 25 micrometers as coating liquid for transparence thermal breaks was prepared, and the heat-reversibility record object of three colors with which it comes to carry out laminating mediation of this thermal break as follows using this was produced. By having used the same white PET film as an example 1 as the base, it sequential-applied, this red coloring liquid and this red lean solution were first, dried on the same conditions as this example, and the 1st heat reversible red recording layer 1 was formed. Next, at intervals of [ of 5mm ] the pitch, UV irradiation of this liquid for thermal breaks was implanted and carried out, it was hardened by screen printing in the shape of a grid, and the transparence thermal break 4 by the glass bead dot was formed so that it might become 27 micrometers of thickness on this red recording layer. Next, on this transparence thermal break, on the same conditions as an example 1, it sequential-applied, this blue coloring liquid and this blue lean solution were dried, and the 2nd heat reversible blue recording layer 2 was formed. And on this blue recording layer, again, UV irradiation of this liquid for thermal breaks was applied and carried out, it was hardened by screen printing, and the transparence thermal break 4 was formed so that it might become 27 micrometers of thickness. Finally, said green coloring liquid and green lean solution were applied and dried on the conditions as an example 1 that it is the same on this transparence thermal break, and the 3rd heat reversible green recording layer 3 was formed, and it ended. In addition, the configuration of the acquired heat-reversibility record object is illustrated to drawing 1 with an example 1.

[0041] And about the heat-reversibility record object which intervenes the transparence thermal break of said three obtained colors, semiconductor laser light was irradiated to each on the same conditions as an example 1, the test of coloring and a discharge was performed, and adiabatic efficiency was checked. Consequently, when each coloring situation was first observed by the eye side, the coloring itself was sensed clearer a little than some [ early and ] for each color rather than the example 1. And chromaticity  $L^*a^*b^*$  of each coloring is measured and it is \*\*\*\* to Table 1 about this again. A more clear thing can be proved in this table. Although  $L^*a^*b^*$  was measured whenever [ coloring / of each color ] when it was attached to \*\*\*\*\* and coloring and a discharge were repeated 150 times, the difference was not seen between the beginnings (Table 1). Moreover, when said three semiconductor laser light was irradiated at coincidence, three colors colored to coincidence in the clear color like the case of monochrome, and it also checked that the total color had decolorized shortly after setting this to 80-degreeC.

[0042] (Example 1 of a comparison) The water-solution 90 weight section of 2.5% of the weight of polyvinyl alcohol was added to 40 weight sections and this, and mixed distribution of what mixed the red color coupler, blue color coupler, and green color coupler of the heat-reversibility used in the example 1 in the amount of division into equal parts was fully carried out (C fluid). And it applied so that it might become 10 micrometers of thickness on the white PET film which used this C fluid in the example 1, and the heat reversible recording layer of 3 color mixing which dries and consists of one layer was prepared.

[0043] Next, sequential spreading was carried out using the same red lean solution, the blue lean solution, and the green lean solution, it dried and the laminating of the laser beam (2 1st, 3) absorption layer of 1-micrometer thickness was respectively carried out to having used it in the example 1 on said heat reversible recording layer.

[0044] Like the example 1, to the heat-reversibility record medium of said three obtained colors, it colored respectively, and it decolorized to it using the laser beam of a semi-conductor (655nm, 780nm, and 830nm), and the coloring situation was seen. As a result, three colors colored almost instantaneous also to the laser beam of which wavelength, and coloring in monochrome was not seen. Carry out respectively independently the laminating of a number equivalent to the color number to color at least of the heat reversible color recording layers, and he makes this color by the laser beam which has the wavelength of a proper in coloring of the recording layer, and it can understand well that there are a heat-reversibility record medium of this invention referred to as to cool and decolorize and a remarkable difference.

[0045]

**[Effect of the Invention]** Since this invention is constituted as aforementioned, the following effectiveness is done so.

[0046] First, it became possible to be able to carry out multicolor coloring in a clear color very quickly by combining at least three laser beams from which wavelength differs to the heat reversible multicolor record medium in which a heat reversible recording layer comes to carry out a laminating and this medium of at least 3 colors as an independent layer respectively, and to decolorize immediately by cooling.

[0047] The periodic duty of degradation of many \*\* and discharges is also small, and a big improvement came to be found by endurance.

[0048] Since it wrote in by the laser beam, it came to be able to carry out a color expression to the detailed part more. The activity in the range larger than the result was attained, and possibility of taking and changing to hard copy also came out.

## CLAIMS

---

### [Claim(s)]

[Claim 1] The heat-reversibility multicolor record medium characterized by coming to carry out the laminating of the three layers of each heat reversible color recording layer of following (A) - (C) at least on a substrate (5).

(A) The heat reversible color recording layer which consists of the 1st heat reversible color coloring layer (1a) and an absorption layer (1b) of the 1st laser beam which has the wavelength for coloring of this coloring layer (1)

(B) The heat reversible color recording layer which consists of an absorption layer (2b) of the 2nd laser beam which has the wavelength for coloring of the 2nd heat reversible color coloring layer (2a) and this coloring layer (2)

(C) The heat reversible color recording layer which consists of the 3rd heat reversible color coloring layer (3a) and an absorption layer (3b) of the 3rd laser beam which has the wavelength for coloring of this coloring layer (3)

[Claim 2] The heat-reversibility multicolor record medium characterized by coming further to carry out the laminating of the transparence thermal break (4) between the layers of the heat reversible color recording layer (1, 2, 3) of at least three layers by which a laminating is carried out in said claim 1.

[Claim 3] The heat-reversibility multicolor record medium according to claim 2 which said transparence thermal break (4) becomes with the detailed glass bead implanted in the shape of a dot by 5-100 micrometers in thickness.

[Claim 4] The heat-reversibility multicolor record medium according to claim 1 or 2 with which the hue in said each heat reversible color coloring layer (1a, 2a, 3a) consists of red, blue, and one of three green colors.

[Claim 5] A heat-reversibility multicolor record medium given in claims 1 and 2 as which said each laser beam is chosen from light with a wavelength of 600-1000nm emitted from semiconductor laser, or any 1 term of 4.

[Claim 6] A heat-reversibility multicolor record medium given in claims 1, 2, and 4 which the absorption layer (1b, 2b, 3b) of each of said laser beam is respectively chosen from with a molar extinction coefficients of 10000 or more infrared absorption agents, and come to contain this, or any 1 term of 5.

# DRAWINGS

Fig. 1

